MOLECULAR MOTION IN A CELLULOSE NITRATE–GLYCERIN TRINITRATE SYSTEM*

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The molecular motion in a number of cellulose nitrates plasticized with glycerin trinitrate was investigated by means of a two-pulse NMR technique over a wide range of temperatures. The experimental results are explained in the light of Resing's theory.

The physical properties of plasticized polymeric systems are influenced to a considerable extent by molecular motion in these systems [1, 2], but only limited information is available in this connection in literature [3, 4]. A pulse NMR technique may be used for investigations of this kind, and in some cases this has enabled authors to observe the motion of the macromolecules separately from that of plasticizer molecules [5]. In this paper we report our investigation of molecular motion in a plasticized polymeric system containing cellulose nitrate (CN) and glycerin trinitrate (GTN), using a pulse NMR spectrometer.

EXPERIMENTAL

The nuclear magnetic spin-spin (T_2) and spin-lattice (T_1) relaxation times were measured with a pulse NMR-spectrometer at a frequency of 19 MHz [6]. The T_1 measurements were carried out with a 90–180° two-pulse sequence, checking the magnetization decay for an exponential relationship. T_2 times of less than 100 μsec were determined from the free induction decay following the 90° pulse; when longer than 100 μsec T_2 values were determined by using the Meiboom–Gill modification [7] of the Carr–Parcell method. A 180° pulse repetition frequency of 5 kHz was used for all measurements of long T_2.

Samples were prepared from commercial cellulose nitrates with nitrogen contents of 11·9 and 13·1%, these being the low nitrogen and high nitrogen (LNCN, HNCN) samples respectively. The plasticizer content of the samples was varied from 25 to 50% by wt. The measurements were carried out with two batches of samples in the temperature range from −100 to +115°. The samples were prepared by mixing the components in an aqueous medium at 50° followed by milling on a laboratory mill, the number of rolls being 25 in all cases.

The nuclear induction decay or the envelope of spin echo signals in the case of the compositions investigated is described by the functions

$$A(t)=A_{0a}\exp\left(-\frac{t}{T_{2a}}\right)+A_{0b}\exp\left(-\frac{t}{T_{2b}}\right) \tag{1}$$

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